Quality Assessment Report for Water Quality Monitoring

October – December 2001



Submitted to the Technical Oversight Committee

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This report is an assessment of the SFWMD laboratory and field sampling in Total Phosphorus (TP) monitoring primarily for the following projects/stations during the last quarter of 2001.

- Conservation Area Inflow and Outflows (CAMB) S12A, S12B, S12C S12D, S333
- Everglades National Park Inflow Monitoring (ENP) S175, S176, S177, S18C, S332, S332D
- Everglades Protection Area (EVPA) LOX3 to LOX16
- Non-Everglades Construction Project (NECP) S334

The lists of qualified data (Table 3) and field sampling quality assessment (Table 4) also include information on stations other than those listed above or other projects since field QCs are collected for trips that include the samples for the stations of interest.

The South Florida Water Management District's Comprehensive Quality Assurance Plan (CQAP) requires analysis of laboratory quality control (QC) samples and the collection and analysis of field QC samples along with routine samples to assess the data quality. Included are the results from a split study with SFWMD and Florida Department of Environmental Protection (FDEP) laboratories for total phosphorus analysis to continually determine comparability of results.

Field Sampling Quality Assessment

Field QC measures consist of equipment blanks (EB), field blanks (FB), split samples (SS) and replicate samples (RS). Table 1 summarizes EB and FB recoveries for all projects and Table 2 summarizes field precision recoveries. Data not meeting the set criteria are flagged using FDEP data qualifier codes.

Field sampling precision was generally acceptable. In cases when the precision exceeded criteria, the affected sample was flagged. A comprehensive list of flagged data for all trips that include samples for CAMB, ENP, EVPA and NECP during this quarter is presented in Table 3.

Based on an audit conducted by District staff on 3/11/02 of Dade County Department of Environmental Resources Management (DERM) sampling team, sample collection procedures were generally acceptable and comply with SFWMD and DEP requirements. The following was a corrective action required of DERM, based on that audit: Use pH calibration standards at the right range. DERM was calibrating using pH7 and 10, while most of the field readings were below pH 7, and therefore, calibration should include pH4 buffer. The following was recommended to improve the integrity of collection: Dates when corrections were made should be indicated on the chain of custody sheet. The District is waiting for DERM's response on this audit report. This collection was for CAMB, ENP, NECP, and 8SQM projects.

Table 1. Field and Equipment Blank Recoveries

Type of Blank	Project	# Blanks collected	% with value <0.004	% with value 0.004-0.008	% with value >0.008	Action Taken
FB	CAMB	444	99.3	0	0.7	Data flagged
	ENP	22	100	0	0	N/A
	EVPA	15	100	0	0	N/A
	NECP	2	100	0	0	N/A
EB	CAMB	327	98.2	0.9	0.9	Data flagged
	ENP	61	95.1	3.3	1.6	Data flagged
	EVPA	48	100	0	0	N/A
·	NECP	3	100	0	0	N/A

Table 2. Field Precision Summary

Project Code	Numbers of pairs	Mean % RPD	Comments
CAMB	77	10.0	Precision exceeded criteria on the following dates: 10/2; 10/30; 11/6; 11/26; 12/11 & 12/12. Affected samples were flagged
ENP	18	13.8	Precision criteria were met. Those above criteria were all <pql.< td=""></pql.<>
EVPA	18	6.8	Precision criteria were met.
NECP	2	0	Precision criteria were met.

Notes

- 1) All TP analyses were conducted by SFWMD laboratory.
- 2) Field precision acceptance criteria: <15%. This criteria is applied only if values >PQL.
- 3) FB and EB acceptance criteria: Must be </=2xMDL.
- 4) Associated samples are flagged when concentrations are low enough as compared to blank values for possibility of contamination.

Table 3. List of Flagged Results

Project	Date Collected	Station	Type	Flag Code	Comments
CAMB	26-Nov-01	S34	SAMP	J3	Failed field precision criteria
	12-Dec-01	S6	RS	Ј3	Failed field precision criteria
	2-Oct-01	C123SR84	RS	Ј3	Failed field precision criteria
	30-Oct-01	S150	RS	Ј3	Failed field precision criteria
	11-Dec-01	S150	RS	Ј3	Failed field precision criteria
	6-Nov-01	S5A	RS	Ј3	Failed field precision criteria
	24-Oct-01	S6	SAMP	J5	Not flow proportional
	23-Oct-01	G123	SAMP	V	Sample associated with positive blank
	23-Oct-01	S9	SAMP	V	Sample associated with positive blank
	27-Dec-01	G123	SAMP	V	Sample associated with positive blank
	27-Dec-01	S11C	SAMP	V	Sample associated with positive blank
	11-Dec-01	S9	SAMP	V	Sample associated with positive blank
	11-Dec-01	S9	SAMP	V	Sample associated with positive blank
	11-Dec-01	G123	SAMP	V	Sample associated with positive blank
	4-Dec-01	S9	SAMP	V	Sample associated with positive blank
	4-Dec-01	S151	SAMP	V	Sample associated with positive blank
	4-Dec-01	S31	SAMP	V	Sample associated with positive blank
	23-Oct-01	G123	EB	V	EB>2xMDL
	27-Dec-01	G123	FB	V	FB>2xMDL
	27-Dec-01	G123	SS	V	Sample associated with positive blank
	27-Dec-01	G123	RS	V	Sample associated with positive blank
	11-Dec-01	S9	EB	V	EB>2xMDL
	11-Dec-01	S9	SS	V	Sample associated with positive blank
	11-Dec-01	S9	RS	V	Sample associated with positive blank
	11-Dec-01	S9	FB	V	FB>2xMDL
	11-Dec-01	S150	EB	V	EB>2xMDL
	4-Dec-01	G123	FB	V	FB>2xMDL
	4-Dec-01	S31	SS	V	Sample associated with positive blank
	4-Dec-01	S31	RS	V	Sample associated with positive blank
ENP	27-Dec-01	S332DAS	SAMP	V	Sample associated with positive blank
	27-Dec-01	S332DAS	EB	V	EB>2xMDL
	27-Dec-01	S332DAS	SS	V	Sample associated with positive blank

Laboratory Quality Control Assessment

Routine laboratory QC samples include QC checks, matrix spikes and precision checks.

The charts presented on the following pages show recoveries from various levels of QC samples for the TP analysis at SFWMD laboratory. Statistical evaluation of precision and matrix spikes recoveries is also included. Portion of or an entire analytical run is generally rejected if QC recoveries are outside the set limits. Data is flagged accordingly if any deficiency is noted after the samples have exceeded the required holding times.

Except for QC5, recoveries for the QC samples are generally within \pm 10% from the true value, which are acceptable. QC5, with a true value of 0.006 mg/L, is less than the practical quantitation limit. Although a wider performance range can be expected at this level, the recoveries are biased on the high end of the chart, 83.3 - 116.7% with a mean of 103.1%.

Organic check is a solution prepared from phytic acid, a stable form of organic phosphate. Recoveries for this check sample are between 96.7 - 101.9%, indicating that the digestion process was effective. The same material is used to do matrix spikes, the mean recovery for which was 102.6%.

The precision target for TP analysis during this period was 5.0% and as the report shows, mean %RPD was 1.02% and 0.76% for low and high level analyses, respectively. The maximum RPD during this period were 3.9% & 3.5% for low & high respectively.

Split and Round Robin Studies

To continually assess comparability of results, the District began splitting samples, collected from the Loxahatchee National Refuge site (EVPA Project), with the Florida Department of Environmental Protection's laboratory. This split study is conducted quarterly. The result of the split study is presented in Table 4 below:

Table 4. Results of 11	split studies between SI	WMD and FDEP	laboratories, 12/3/01.
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Station	Sampling Date	Type	SFWMD		FDEP		Difference	RPD %	Comments
			Field #	TP, mg/L	Field #	TP, mg/L	(SFWMD-FD)	EP)	
LOX6	12/3/01	EB	P10071-1	<0.004	P10070-1	<0.004	0.000	0.0	
LOX6	12/3/01	SS	P10071-2	0.006	P10070-2	0.006	0.000	0.0	
LOX7	12/3/01	SS	P10071-6	0.007	P10070-3	0.008	-0.001	13.3	
LOX8	12/3/01	SS	P10071-7	0.008	P10070-4	0.008	0.000	0.0	
S5AD	12/3/01	FB	P10071-14	< 0.004	P10070-5	< 0.004	0.000	0.0	
S6D	12/4/01	SS	P10773-2	0.032	P10070-6	0.036	-0.004	11.8	
LOX12	12/4/01	SS	P10073-4	0.006	P10070-7	0.007	-0.001	15.4	
LOX16	12/4/01	SS	P10073-6	0.006	P10070-8	0.007	-0.001	15.4	

Both laboratories obtained acceptable blank (EB and FB) results. For S6D split, which is the only set of results > PQL, the RPD between the results is 11.8%.

A copy of Everglades Round Robin 10 results showing the District's laboratory performance, as compared with the other participating laboratories is also provided in this report. Also provided in this report is the result of District's own performance evaluation program (Table 5). This program is coordinated by the District's Quality Assurance Section. The District's laboratory also obtained excellent ratings in USGS Round Robin studies around this time period.

Table 5. Results of TP Performance Evaluation studies coordinated by SFWMD QA Section, 3/2001

Lab	Blank	Known QC	Field	Field	Spiked Field	Spike
			Sample 1	Sample 2	Sample 1	Duplicate
	<mdl< th=""><th>0.050</th><th>0.021</th><th>0.046</th><th>0.069</th><th>0.066</th></mdl<>	0.050	0.021	0.046	0.069	0.066
TVA Lab	< 0.002	0.050	0.018	0.038	0.072	0.065
SFWMD Lab	< 0.004	0.047	0.022	0.046	0.069	0.069
DERM Lab	< 0.001	0.047	0.022	0.046	0.069	0.066
PPB Lab	< 0.004	0.050	0.021	0.050	0.070	0.070
ELAB Lab	< 0.004	0.046	0.018	0.043	0.066	0.065
FDEP Lab	< 0.004	0.048	0.023	0.051	0.070	0.073
Sanders Lab	< 0.010	0.144	0.135	0.164	0.179	0.182
USGS Lab	0.010	0.040	0.020	0.040	0.050	0.050
USBio Lab	< 0.0081	0.042	0.016	0.051	0.063	0.061
Collier Cty Lab	< 0.010	0.040	0.020	0.040	0.070	0.070
Lee Cty Lab	< 0.050	0.040	< 0.050	< 0.050	0.060	0.060
FIU-SERP Lab	0.010	0.050	0.030	0.050	0.080	0.070

Round Robin TP-10

Results									1									
Laboratory									N S	n c			CDK1			-	113	
		F2			F4	- 1		3.3	010	٥	2500	1000	000	000	0.0084111	0.0084 11	0.008111	0 0081 11
	0.022	0.022	0.022	0.010	0.012	0.011	0.0081 U	0.043	0.043	0.043 8	0.043 13	9	18	12 2	6	11	10	14
US biosystems, inc FL Dept. of		0	2					0 064	0.050	0.053	0.50	0.033	0.032	0.034	1 900 0	0.0051	0.006	0.0061
Environmental	0.029	0.025	0.028	10.010	9.010	4	- 600.0	7	16	13	11.5	2	12	8	Ω.	15	10	14
LICIECTION	0000	0 0 0	0 0 0 0	0.007	0.007	0.010	0.005 U	0.041	0.044	0.041	0.037	0.024	0.010	0.020	0.005 U	0.005 U	0.005 U	0.005 U
TestAmerica, Inc	15	8	10	5	7	13	3	16	17	-	12	=	18	6	4	4	2	9
IFAS Everglades	0.017	7600	0.022	0 008	0 008	900 0	0.008	0.039	0.044	0.042	0.038	0.026	0.023	0.029	0.004	0.004	600.0	0.008
Research & cubcation	5 2	15	13	14	9	16	3	5	18	8	17	12	=	-	7	6	4	2
Metro Dade County	0.00	0.028	0.028	0.013	0.013	0.011	0.013	0.050	0.051	0.050	0.050	0.032	0.034	0.032	0.010	0.007	0.008	600.0
Resources Mot.	9		13		4	5	18	6	5	3	2	12	-	14	15	11	17	16
	0.024	0.026	0.026	0.0088	6900.0	0.0040 U	0.0095	0.045	0.046	0.047	0.046	0.032	0.030	0.029	0.0040 U	0.0040 U 17	0.0040 U	0.0040 U
ELAB	4	10	12	2	80	13	13	5	0 00	4 6	9600	5000	0000	7000	9000	9000	0 005	9000
STI Mismi Inc	0.014	0.021	0.020	0.010	3 3	17	13	0.040	18	5 4	4	11	5	8	5	16	9	-
UF/IFAS-Wetlands															000	0	000	900
Biogeochemistry	0.025	0.025	0.025	0.010	0.010	0.010	0.010	0.047	0.046	0.046	0.046	0.031	0.030	0.031	0.006	0.00	11	8 %
Laboratory	18	9	14	2 5	13	6	200	77	200	- 0	8700	000	0000	0.030	0 006 1	1 900 0	0.0071	0.0061
DB Environmental	0.027	0.027	0.026	0.010	0.010	0.010	0.0.0		1.040	16		5 =	4	10	2	13	6	6
Laboratones, Inc.	2000	1000	200	000	9000	600 0	600 0	0.051	0.049	0.046	0.048	0.024	0.024	0.024	600.0	0.014	0.024	0.004
Evergiades Laboratories,		15	16	13	12	10	18	5	2	11	8	9	4	7	6	4	1	17
PPB Environmental	0.028	0.027	0.027	0.012	0.010	0.010	0.013	0.050	0.049	0.049	0.048	0.031	0.032	0.032	0.008	0.008	0.000	18
Laboratories, Inc.	3	9	16	-	14	5	1/	6,0	4 0	70,00	- 0	000	2000	0000	2000	2 000	0.0051	1 900 0
Short Enivronmental	0.028	0:030	0.026	0.015	0.011	0.010	0.010	0.049	3	0.049	0.049	17	12	8 8	2 2	9.00	16	11
Laboratories	200	5000	2000	200	800	9000	2000	0.045	0.045	0.041	0 044	0.029	0.028	0.029	0.003	0.002 U	0.002 U	0.002 U
TVA Environmental	0.023	0.020	8	2.000	17	9	1.5	, ,	2 2	16	13	18	5	4	-	14	3	10
II.S. Sugar Corp South	0.029	0.029	0.029	0.015	0.015	0.015	0.015	0.050	0.050	0.050	0.050	0.031	0.031	0.031	0.011	0.011	0.011	0.011
Bay Laboratory	ဖ	17	13	3	S	10	18	4	12	80	6	4	=	15	_	-	16	7
Harbor Branch	0 0313	0.0251	0.0312	0.00827	0.00384	0 0135	0.0178	0.0570	0.0459	0.0541	0.0490	0.0200	0.0276	0.0339	0.00254	0.00818	0.00731	0.00607
I aboratory	5 6	9	8	2	17	13	Ξ	9	15	7	3	18	-	12	16	5	14	4
	0.028	0.028	0.029	0.012	0.012	0.012	0.012	0.050	0.050	0.050	0.051	0.030	0.021	0.030	0.007	0.008	0.008	0.007
U.S. Geological Survey	10	12	4	2	18	9	14	8	7	8	13	1	200	/-	200	2 5	- 6	0011
Duke-School of the	0.031	0.031	0.032	0.016	0.016	0.016	0.016	0.054	0.052	0.052	0.052	0.036	0.035	18 6	17	- 6	10.7	
Environment	4		13	16	15	0	, [7100	1000	- 00	0 0 0 0 0	200	0,00	010	9100	0.00	0.028	0.018
ogsocial To	0.039	0.031	0.027	0.015	0.020	0.013	0.016	0.045 16	3 (2)	15	 	4 4	2 2	11	13	14	17	12
South FL Water Mgt.	0.027	0.026	0.026	0.010	0.011	0.011	0.011	0.050	0.049	0.048	0.050	0.031	0.031	0.030	0.005	0.006	900.0	900.0
District	۵	٥	4	2	_	7		2		2								

Glossary

Equipment blank (EB). Analyte-free water that is processed on-site through all sampling equipment used in routine sample processing. EB values are indicative of effectiveness of decontamination process.

Field

blank (FB). Analyte-free water that is poured directly into the sample container on site during routine collection, preserved and kept open until sample collection is completed for the routine sample at that site. FB values are indicative of environmental contamination on site.

Split sample (SS). A second sample collected from the same sample obtained from the same sampling device. Results for SS are compared with routine sample results; agreement between these two results is mostly an indication of laboratory precision.

Replicate sample (RS). A second sample collected from the same source as the routine sample, using the same sampling equipment. RS data are compared to routine sample to evaluate sampling precision.

Precision. The agreement or closeness between two or more results and is an indication that the measurement system is operating consistently and is a quantifiable indication of variations introduced by the analytical system over a given time period.

Accuracy. The agreement between the actual obtained result and the expected result. QC check samples having known or "true" value are used to test for the accuracy of a measurement system.

Method Detection Limit (MDL). The smallest concentration of an analyte of interest that can be measured and reported with 99 percent confidence that the concentration is greater than zero. The MDL's are determined from the analysis of a sample in a given matrix, using accepted sampling and analytical preparation procedures, containing the analyte at a specified level. The MDL is determined by the protocol defined in section 40 CFR Part 136, Appendix B as established by the EPA.

Practical Quantitation Limit (PQL). The smallest concentration of an analyte of interest that can be quantitatively reported with a specific degree of confidence. Generally, the PQL is 12 times the standard deviation that is derived from the procedure used to determine the MDL, or can be assumed to be 4 times the MDL.

Relative Standard Deviation (RSD). A measurement of precision, used when comparing more than two results. It is calculated as: %RSD = [Std. Deviation/Mean]*100

Relative Percent Difference (RPD). A measure of precision, used when comparing two values. It is calculated as: %RPD = [Value1-Value2]/Mean * 100.